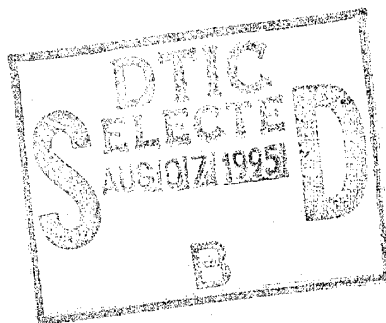


**Technical Report
1024**

Temperature Dependence of Large Polaron Superconductivity

G.F. Dionne



18 July 1995

Lincoln Laboratory

MASSACHUSETTS INSTITUTE OF TECHNOLOGY

LEXINGTON, MASSACHUSETTS



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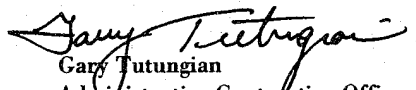
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LINCOLN LABORATORY

**TEMPERATURE DEPENDENCE OF
LARGE POLARON SUPERCONDUCTIVITY**

G.F. DIONNE
Group 63

TECHNICAL REPORT 1024

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ABSTRACT

The theory based on covalent electron transfer (CET) between the $d_{x^2-y^2}$ orbitals of mixed-valence Cu ions that was introduced previously to explain the variation of critical temperature T_c with chemical composition and the temperature dependence of high- T_c superconductor properties is modified to reflect lattice-vibration scattering of the large polarons that dominate the electrical conductivity of these compounds at low temperatures. One result of this refinement is a clearer picture of the dependence of electron hopping activation energy on crystal-field parameters. A generalization of the earlier exponential "two-fluid" model is introduced to describe more accurately the high rate of change in supercarrier density with temperatures in the regime where T approaches T_c . This new model can provide additional insights from the fitting of theory to data. At the lowest temperatures, supercarrier densities may be approximated by a linear function of temperature if T_c values are large. For lower- T_c superconductors the dependence is more typically exponential. With these improvements, precise fits to penetration depth versus temperature measurements for high-purity YBCO single crystals were obtained, as well as more accurate agreement with critical (transport) current density versus temperature data for thin films. Projections of critical current densities as a function of reduced temperature $t = T/T_c$ are offered for the highest T_c materials predicted by this theory. Parameter values desired for optimum superconductor properties are reexamined.

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1. INTRODUCTION

From a study of the origin of coherent charge transfer originating from large polaron conduction in layered cuprates at low temperatures, a theory of superconductivity based on covalent electron transfer (CET) was developed [1,2]. The fundamental concept that was used to determine the transition temperature was the statistical partitioning of carriers between polaronic (adiabatic and coherent) and thermally activated (incoherent) hopping. Where the electronic bandwidth is much greater than the polaron trap energy, i.e., $b \gg E_{\text{hop}}$, it is assumed that all carriers are large polarons that can undergo spontaneous delocalization over distances of several lattice parameters, unless activated to hopping by a thermal energy transfer. In the *p*-type cuprates, charge transfer occurs between partially filled 3*d* shell Cu^{3+} (d^8) ions and the host Cu^{2+} (d^9) ions; b is determined principally by the covalent coupling of the Cu 3*d*_{*x*-*y*}² orbital lobes with those of the 2*p* oxygen states. In cases where *n*-type charge transfer occurs between the filled 3*d* shell Cu^{1+} (d^{10}) ions and the host Cu^{2+} (d^9) ions, the natural overlap of the 3*d* and 4*s* bands can permit a larger contribution from the spherically symmetric 4*s* wave function. This overlap would manifest itself as a reduced anisotropy in the basal planes of the layered cuprates.

Polaron trap energies arise from electrostatic fields of the ionic bond and the crystal field interaction between cation and ligand. As determined from electron hopping activation energies, E_{hop} is generally on the order of 10^{-2} eV where spin polarization energy is not involved, e.g., mixed valence Ti, Bi, and Tl compounds. For oxides of the 3*d* transition metal series, antiferromagnetism can increase the stabilization of the carrier in its trap by at least two orders of magnitude. For reasons that are related to the magnetic dilution from zero-spin ($S = 0$) Cu^{3+} and Cu^{1+} ions [3], the breakdown of long-range antiferromagnetic order reduces the activation energy E_{hop} to values below 10 meV. Since the narrowing of b with increasing temperature is not an issue as long as the large polaron condition $b \gg E_{\text{hop}}$ is satisfied, the only temperature dependence of the polaron supercarrier density n_s arises from a Boltzmann-type partition fraction of hopping carriers, which become dominant where $E_{\text{hop}}/kT \ll 1$. Except for the spatial ordering of the polaron supercarriers, which is necessary to satisfy the London $\nabla n_s = 0$ condition, this temperature dependence is analogous to that of the collective carrier distribution of a degenerate semiconductor.

In this report an additional temperature-dependent factor is introduced to account for the scattering of polaron carriers by lattice vibrations. This scattering effect does not reduce the density of carriers but disrupts the formation of coherent chains of polaronic carriers that are the basis of the superconducting state. Moreover, the two-fluid function developed previously [2,4] is placed in a more general format that makes it sensitive to specimen purity and homogeneity.

2. THEORETICAL DETERMINATION OF T_c

For a system of N carriers per unit volume, the fraction of supercarriers n_s is determined by a series of probabilities [2]: (a) that of polaronic conduction, i.e., not thermally activated (hopping) $P_{\text{pol}} = [1 - \exp(-E_{\text{hop}}/kT)]$, (b) that of polaron isolation $P_{\text{isol}} = 1 - 4\beta x$, where $0 \leq \beta \leq 1$ is a polaron dispersal parameter, and (c) the quantum mechanical transfer probability $P_{\text{trans}} = \eta$ derived from the overlap of $3d_{x^2-y^2}$ and $2p$ wave functions (p -type case). The resulting relation became:

$$\frac{n_s}{N} = P_{\text{trans}} P_{\text{isol}} P_{\text{pol}} \quad (1a)$$

$$= \eta(1 - 4\beta x) \left[1 - \exp\left(\frac{-E_{\text{hop}}}{kT}\right) \right] \quad (1b)$$

The original expression for η was derived from a molecular-orbital model that included a $\text{Cu}^{2+}\text{-O}^{2-}\text{-Cu}^{2+}$ superexchange calculation, from which:

$$\eta = 1 - \Omega \quad , \quad (2)$$

where $W = \Delta E/b$, with b representing the exchange integral energy derived from the molecular-orbital theory of covalent bonding and $\Delta E = \Delta E_0 \Psi$ describing the electrostatic energy of the polaron trap. $\Delta E_0 = (e^2/Ka)$, where K is the effective dielectric constant, a is the minimum separation between Cu sites in the x - y plane (lattice parameter), and Ψ is a function of carrier concentration x that has been modeled in Dionne [1,2] to reflect four and two interacting polarons, respectively. In its simplest approximation $\Psi = 1 - 2x$.

The parameter b was originally chosen as 0.43 eV based on a calculation derived from Anderson's theory of superexchange in transition-metal oxides [1,2]. For the following analysis, it has been found appropriate to consider this quantity as a slowly decreasing function of polaron concentration x . For the layered cuprates, the following relation is used to obtain T_c values that fit experiment:

$$b = b_0(1 - \alpha x) \quad , \quad (3)$$

where standard values of $b_0 = 0.36$ eV and $\alpha = 0.5$ eV based on fits to data for $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ (YBCO). Since b depends directly on the overlap of orbital wave function lobes [2], this dependence of b on x is at least qualitatively plausible because of the anticipated reduction in covalent linkages due to the absence of e_g orbital bond linkages that occurs when either Cu^{3+} or Cu^{1+} is formed.

Equation (2) will now be viewed as an approximation to the more general relation:

$$\eta = \exp(-\Omega) \quad , \quad (4)$$

which will be used in future analysis.

It is now appropriate to recall the carrier threshold $x_s = x_t$ (typically < 0.1) for superconductivity [2] as:

$$\begin{aligned} x_t &= \frac{(2\Omega-1)}{4\Omega} & \text{for } \Omega \geq 0.5 \\ &= 0 & \text{for } \Omega \leq 0.5 \end{aligned} \quad (5)$$

A revised expression of Equation (1) for the supercarrier fraction then becomes:

$$\frac{n_s}{N} = \frac{x_s}{x} = \exp(-\Omega)(1 - 4\beta x) \left[1 - \exp\left(-\frac{E_{\text{hop}}}{kT}\right) \right] \quad (6)$$

To solve for T_c as worked out originally in Dionne [1], let $x_s = x_t$ according to Equations (5) and (6). With the transfer probability now expressed exponentially, a new set of theoretical curves of T_c as a function of x are plotted in Figure 1 for the parameters in Table 1. For p -type cuprate superconductors, note that E_{hop} increases from a relatively low value of 4 meV to values of 12 meV as the strength of the axial crystal-field component increases with the change in the Cu environment from distorted octahedral to pyramidal to planar. The relation between the magnitude of E_{hop} and the oxygen coordination about the Cu ions is diagramed in Figure 2, which depicts the increase in E_{hop} as a progressive destabilization of the upper $d_{x^2-y^2}$ orbital state with increasing axial (tetragonal) crystal-field strength Δ . These larger values of Δ have the effect of further stabilizing the low-spin ($S = 0$) state of Cu^{3+} ions [1–3]. Where the transfer orbital contains a significant $4s$ wave function component, as in the case of n -type cuprates or metals, the influence of this crystal-field splitting would be correspondingly reduced. Consequently, E_{hop} and T_c values would be smaller. The improvement in polaron dispersal also serves to enhance T_c by allowing larger concentrations of polarons to participate in supercurrents.

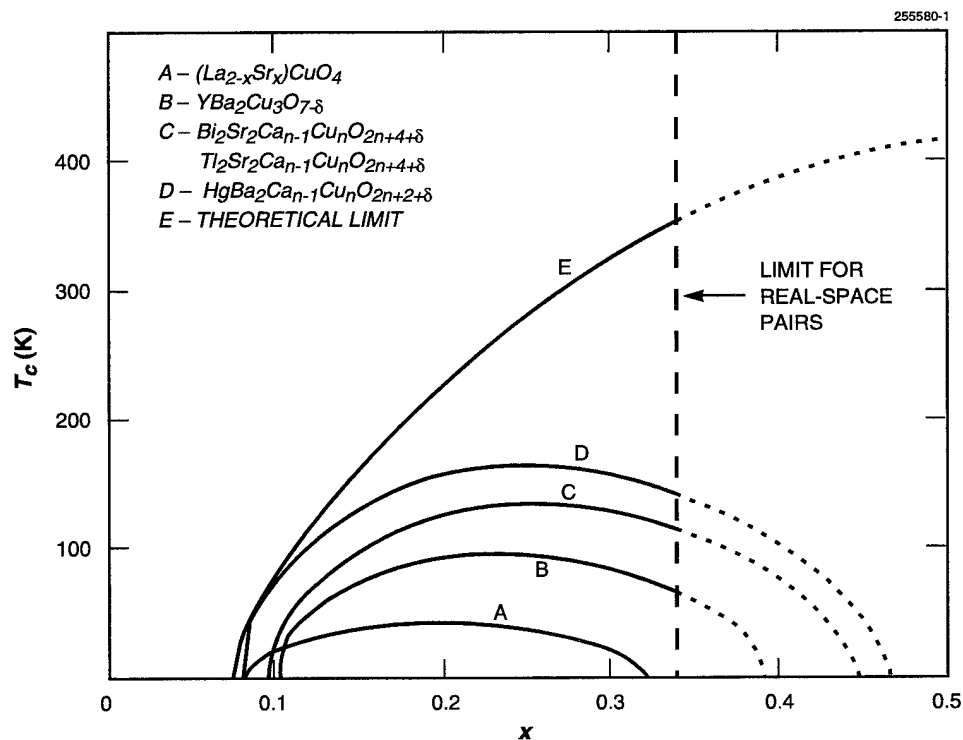


Figure 1. CET theory projection of critical temperatures for cuprate superconductors as functions of polaron charge density and the degree of polaron charge dispersal. Curve A is the $(\text{LaSr})_2\text{CuO}_4$ system with distorted octahedral coordinations, curve B is $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ with pyramidal coordinations, curve C is the Tl/Bi/Hg cuprates with planar coordinations, curve D is curve C with enhanced b , and curve E is a proposed theoretical limit with $b = 0$.

TABLE 1
Parameters for Calculating T_c in Figure 1

Curve	E_{hop} (meV)	β	K^*	a (Å)	b_0 (eV)
A	4	0.5	16	4	0.37
B	10	0.45	16	4	0.36
C	12	0.4	16	4	0.36
D	12	0.4	16	4	0.37 [†]
E	12	0	16	4	0.36

*Effective values of K determined from the standard relation $(1/K_{\text{optical}} - 1/K_0)^{-1}$. For these compounds, $K_0 \approx 25$ and $K_{\text{optical}} \approx 10$ (estimated).

[†]Increased b_0 represents the effect of a larger orbital overlap due to increased pressure used in sample preparation.

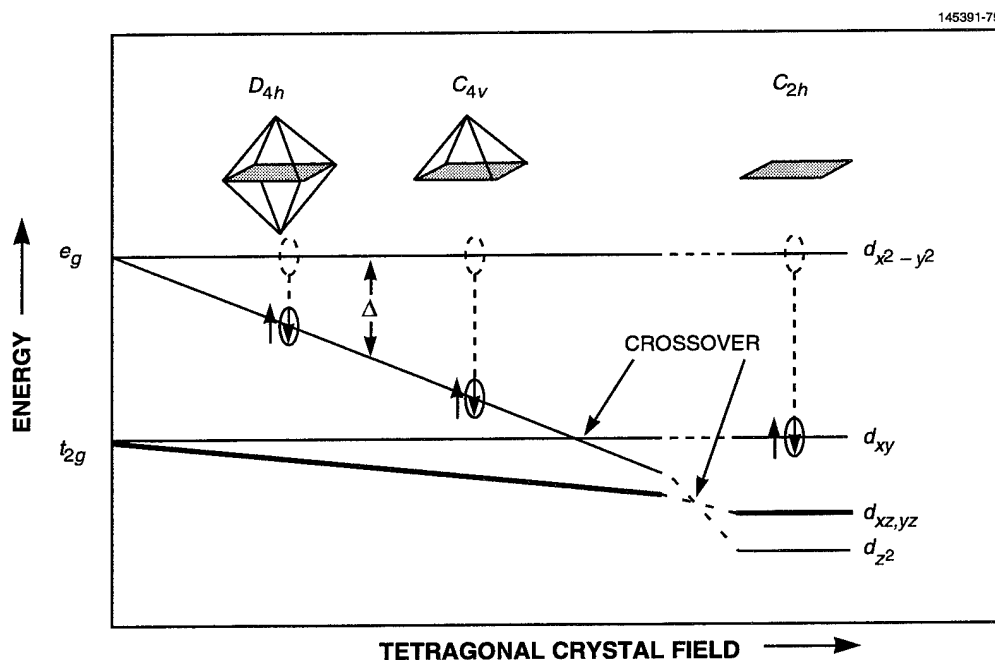


Figure 2. Growth of the $\text{Cu}^{3+} d^8$ low-spin state ($S = 0$) stabilization by e_g doublet splitting as the tetragonal crystal-field component progresses through distorted octahedron (D_{4h}) \rightarrow pyramid (C_{4v}) \rightarrow plane (C_{2h}).

Projections of T_c for the hypothetical case of $E_{\text{hop}} = 12$ meV and $b = 0$ suggest that T_c may reach values in excess of 300 K. The transfer integral b , which may be artificially increased by applying high pressure to increase the overlap of the covalent bonding orbitals, can enhance T_c of Tl/Bi-class compounds to levels above 150 K by raising b_0 from 0.36 to 0.37 eV. Critical temperatures in this regime have been reported for $\text{HgBa}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ samples prepared under extreme pressure [5].

3. POLARON SCATTERING BY LATTICE VIBRATIONS

Electronic conduction in metal oxides with mixed-valence transition-metal ions is typically polaronic at low temperatures, where the carriers are "dressed" by local lattice adjustments to accommodate the change in ionic size and electrical charge at the isolated carrier site. According to the ideas set forth in the Holstein treatise [6], polarons exist in an ionic compound as a result of the covalent bonding component that broadens the electronic energy level of the outer electron into a band of width b . In general, these bandwidths are smaller than the carrier trap or activation energy, i.e., $b < E_{\text{hop}}$, so that the covalent transfer or tunneling probability is proportional to the b/E_{hop} ratio. As temperature increases, the phonons serve to stabilize the carrier in its trap by increasing its lifetime, thereby reducing the influence of the covalent interaction. As a result, the phonons tend to enhance carrier localization by having the effect of narrowing the polaron band (which is the electronic band narrowed by phonons) and restricting the polaron range to a single lattice parameter, i.e., creating a small polaron. Eventually, the band-narrowing will remove the covalent influence and polaron activity altogether, allowing incoherent hopping to take over as the principal conduction mechanism of these basically ionic compounds.

For high- T_c superconductors, however, neither electron hopping nor small polarons will enable the required energy-free charge transport because of the dependence on phonon interactions. Large polarons are necessary for conduction with a coherence length of several lattice parameters, and this situation requires that $b \gg E_{\text{hop}}$. In this case, isolated carriers may move spontaneously over several lattice parameters, limited only by the electrostatic attraction between carrier and fixed-site charge at the impurity site or vacancy that created the polaron, i.e., the other half of a flexible dipole. Typically, b is of the same magnitude as E_{hop} ($\sim 10^{-1}$ eV) and strictly a function of the covalent parts of the chemical bonding of the particular compound. As a consequence, large polarons can be created only by reducing E_{hop} . Two situations where large polarons are possible through lowering E_{hop} to a range below 10^{-2} eV by eliminating the magnetic component of the trap energy are:

1. The spins of both transfer ions are aligned ferromagnetically with each other and with those of the surrounding lattice. Under these conditions, the exchange stabilization is the result of electron delocalization through superexchange by covalent interaction with oxygen. Consequently, the stabilization actually drives rather than impedes the charge transfer. This process occurs with $\text{Mn}^{3+}(d^4) \leftrightarrow \text{Mn}^{4+}(d^3) + e^-$ ferromagnetic couplings in $(\text{La}^{3+}_{1-x}\text{A}^{2+}_x)[\text{Mn}^{3+}_{1-x}\text{Mn}^{4+}_x]\text{O}_3$ compounds that feature large magnetoresistance effects at the Curie temperature. For $x < 0.5$, the ferromagnetism is reinforced because the $\text{Mn}^{3+}\text{-O}^{2-}\text{-Mn}^{3+}$ superexchange is also ferromagnetic through the influence of a quasi-static Jahn-Teller effect.¹

1. The complexities of the various superexchange interactions involving the different valence states of the Mn ions were examined in J.B. Goodenough, A. Wold, R.J. Arnett, and N. Menyuk, "Relationship between crystal symmetry and magnetic properties of ionic compounds containing Mn^{3+} ," *Phys. Rev.* **124**, 373 (1961).

2. One of the transfer ions has zero-spin and the lattice is magnetically disordered. In this case, there is no internal exchange stabilization gained from satisfying the Hund's rule spin polarization requirement, and neither ion has an exchange commitment to its lattice environment. Therefore, there is no static exchange stabilization of any kind. This condition is precisely that of the $\text{Cu}^{2+}(d^9) \leftrightarrow \text{Cu}^{3+}(d^8)$ zero-spin + e^- transfer of the superconducting layered cuprates discussed in Dionne [1,2].

Both situations are readily identifiable by the metallic nature of the resistivity at low temperatures.

For a material with x carriers per formula unit of dimension a , separation between polaron sources $L_p = a/x$. If this distance is treated as a mean free path for coherent transfer of carriers between large polaron cells, scattering by lattice vibrations may decrease the density of available supercarriers according to:

$$\Delta n_{sv} = -n_{sv} \left(\frac{L_p}{\langle \lambda_v \rangle} \right) = -n_{sv} \left(\frac{a}{x} \right) \left(\frac{1}{\langle \lambda_v \rangle} \right) \quad (7)$$

Since $1/\langle \lambda_v \rangle \approx (1/\lambda_D)(T/\Theta_D)$, where λ_D and Θ_D are the respective Debye wavelength and temperature, and $\Theta_D \approx h\nu_D/k$ with the Debye frequency expressed in terms of the acoustic phonon velocity as $\nu_D = v_a / \lambda_D$, Equation (7) may be reduced to:

$$\Delta n_{sv} = -n_{sv} \left(\frac{a}{x} \right) \left(\frac{k}{h} \right) \left(\frac{T}{v_a} \right) \quad (8)$$

where $v_a \approx a(C/M)^{1/2} \approx (Y/\rho_\delta)^{1/2}$. The variables involved in this approximation are the lattice elastic force constant C , the effective atomic mass M , the Young's modulus Y , and the mass density ρ_δ .

After solving the simple differential equation, a lattice scattering probability may be defined:

$$P_{\text{latt}} = \frac{n_{sv}}{N} = \exp \left(-\frac{\zeta T}{x} \right) \quad (9)$$

where $\zeta = (k/h)(a/v_a)$. For the superconducting cuprates, $a \approx 4 \times 10^{-8}$ cm, $v_a \approx 6.5 \times 10^5$ cm/s, and $\zeta \approx 1.3 \times 10^{-3}$ K $^{-1}$. In terms of the reduced temperature:

$$P_{\text{latt}} \approx \exp \left[-\left(\frac{\zeta}{x} \right) T_c t \right] \quad (10)$$

The scattering probability would be significant where T_c is large but less important with lower- T_c materials, e.g., metal and intermetallic compounds.

4. GENERALIZED TWO-FLUID FUNCTION

In the foregoing analysis, an expression for the density of available supercarriers n_s was calculated as a function of the total carrier density N . However, the variable n_s does not represent the actual carriers participating in the supercurrents because only an effective fraction (n_{se}/N) of these polarons will be capable of such ordered linkages at any time for at least two reasons. First, scattering by lattice vibrations will cause deflections or misdirections of the carriers, particularly as the temperature increases and the average wavelength becomes shorter; second, inhomogeneities arising from chemical impurities or microstructural inhomogeneities will prevent a general onset of complete supercurrent near T_c . Only at $T = 0$ may one reasonably assume that $n_{se} = n_s$. A general function capable of representing the growth of supercurrent near T_c may be derived as follows:

$$n_{se}(T) = n_s(T) - n_t(T) \quad , \quad (11)$$

where the threshold supercarrier density $n_t(T) = n_t(T_c)[1 - n_{se}(T)/n_s(0)]$. Upon substituting this relation into Equation (11), the result is:

$$F_1 = \frac{n_{se}(T)}{n_s(0)} = \frac{n_s(T)}{n_s(0)} - \frac{n_t(T_c)}{n_s(0)}[1 - F_1] \quad (12)$$

or

$$F_1 = \frac{n_s(T) - n_t(T_c)}{n_s(0) - n_t(T_c)} \quad . \quad (13)$$

Based on the logic of Equation (12) the general relation may be written as:

$$F_m = \frac{n_s(T)}{n_s(0)} - \frac{n_t(T_c)}{n_s(0)}[1 - F_1]^m \quad (14a)$$

or

$$F_m = \frac{n_s(t)}{n_s(0)} - \frac{n_t(1)}{n_s(0)}[1 - F_1]^m \quad , \quad (14b)$$

where $t = T/T_c$. If $W = E_{hop}/kT_c$, the simple two-fluid relation of Equation (12) may be expressed as:

$$F_1 = 1 - \exp\left(W - \frac{W}{t}\right) \quad , \quad (15)$$

which is the original relation from the CET model [2,4]. The general version of Equation (14) becomes:

$$F_m = 1 - \exp\left(-\frac{W}{t}\right) - [1 - \exp(-W)][\exp(W - \frac{W}{t})]^m \quad . \quad (16)$$

To illustrate the influence of the parameter m , Equation (16) is plotted in Figure 3 as a function of t with $W = 1.25$ for values of m ranging from 1 to 100. In the limiting case $m \rightarrow \infty$, the onset of the

superconducting state would be sudden and complete as $t \rightarrow 1$. This situation would be ideal and require perfect structural homogeneity and optimum dispersal of polaron sources. Therefore, m can be treated as a material quality parameter.

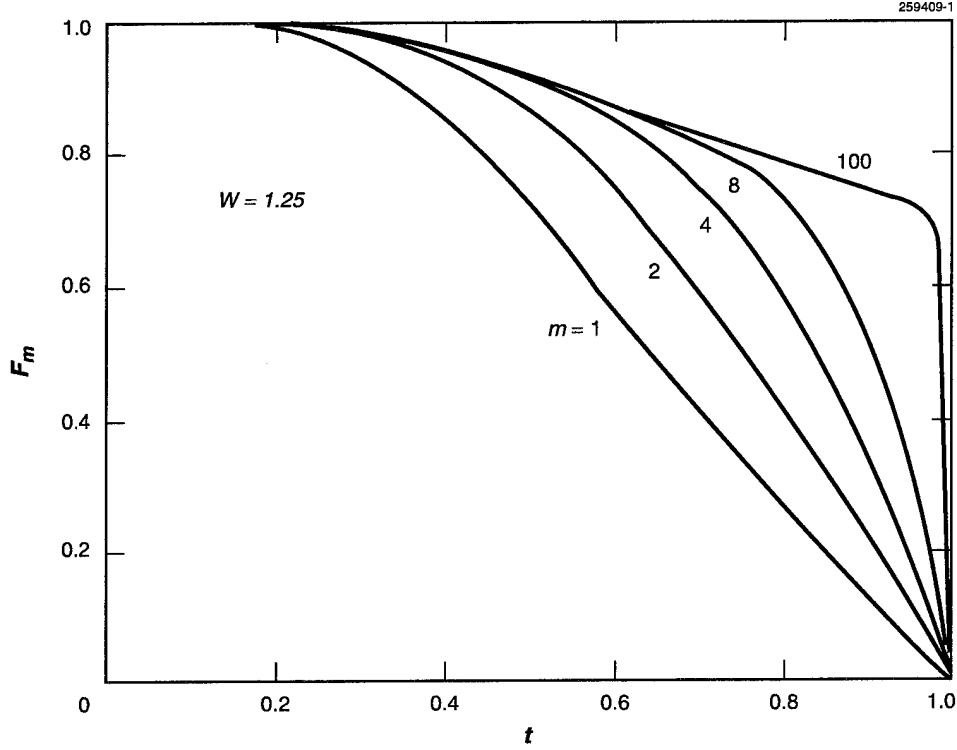


Figure 3. Two-fluid function F_m for $W = 1.25$ and $m = 1, 2, 4, 8$, and 100 .

When the lattice scattering probability factor P_{latt} of Equation (10) is included, the carrier variables are redefined as:

$$\begin{aligned}
 n_s(t) &= N \exp\left(-\frac{\zeta T_c t}{x}\right) \exp(-\Omega)(1 - 4\beta x) \left[1 - \exp\left(-\frac{W}{t}\right)\right] , \\
 n_s(0) &= N \exp(-\Omega)(1 - 4\beta x) , \\
 n_s(1) &= N \exp\left(-\frac{\zeta T_c}{x}\right) \exp(-\Omega)(1 - 4\beta x) [1 - \exp(-W)] .
 \end{aligned} \tag{17}$$

For the YBCO case, $x = 0.25$, $T_c = 93$ K, $W = 1.25$, and Equation (10) reduces to $P_{\text{latt}} \approx \exp(-t/2)$. The general two-fluid function of Equation (14b) is plotted in Figure 4 for the same range of m values with the data of Bonn et al. [8]. In Figure 5, the inverse ratio $[n_{se}(0)/n_{se}(t)]^{1/2} = F_m^{-1/2}$ (which represents the temperature variation of the London penetration depth) is plotted for the same set of parameters, except that T_c is reduced slightly to 90 K and compared with the data selected from Mao et al. [9]. For $m = 8$ in both cases, excellent agreement was obtained with the data that were derived from microwave measurements of penetration depth on nearly perfect single crystal (s.c.) specimens. Figure 6 presents an interesting comparison between theory and experiment for a YBCO textured film. From the data of Porch et al. [10], agreement is established for $m = 4$ at larger t values, but a growing departure is apparent at low t values. The failure to produce a closer fit at low t could be accounted for by a depletion in the long-wavelength phonon populations due to the presence of grain boundaries along longitudinal paths, as well as the submicrometer-scale thickness of the film. The absence of linearity in the slope near $t = 0$ could result, for example, from an inverse quadratic relation between $\langle \lambda_v \rangle$ and T , i.e., $1/\langle \lambda_v \rangle \approx (1/\lambda_D)(T/\Theta_D)^2$ where $T \ll \Theta_D$, thereby introducing a T^2 dependence to the exponent of Equation (9). The parameters used in these computed temperature-dependent properties and those to follow are summarized in Table 2.

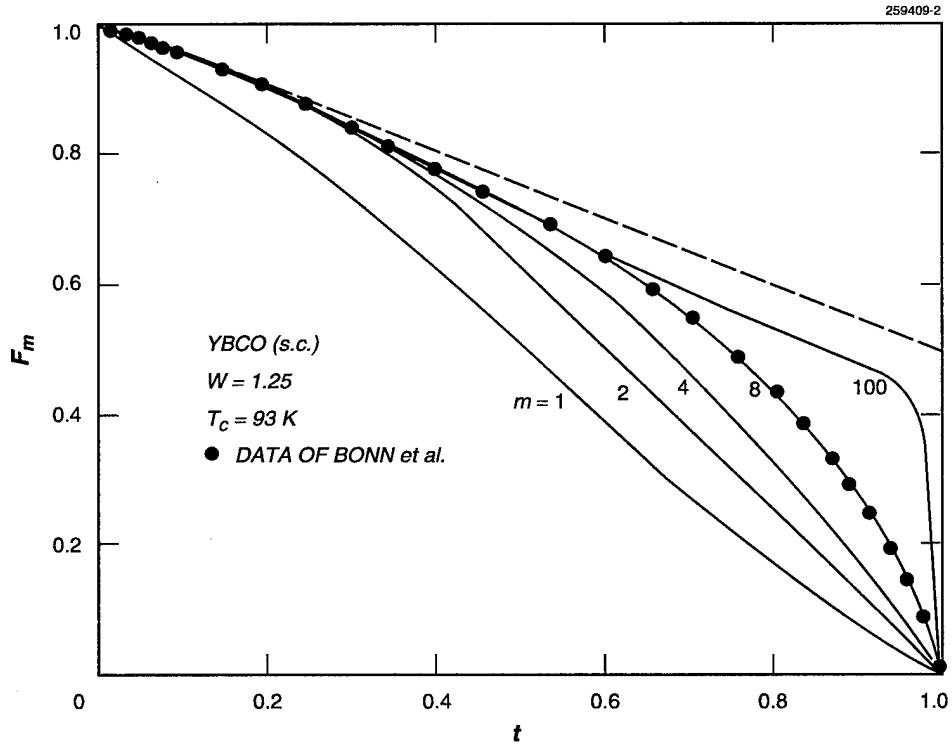


Figure 4. Two-fluid function F_m with phonon scattering included for $W = 1.25$ and $m = 1, 2, 4, 8$, and 100 . In this case, the YBCO parameters of $x = 0.25$ and $T_c = 93$ K are used. Single-crystal data are from Bonn et al. [8].

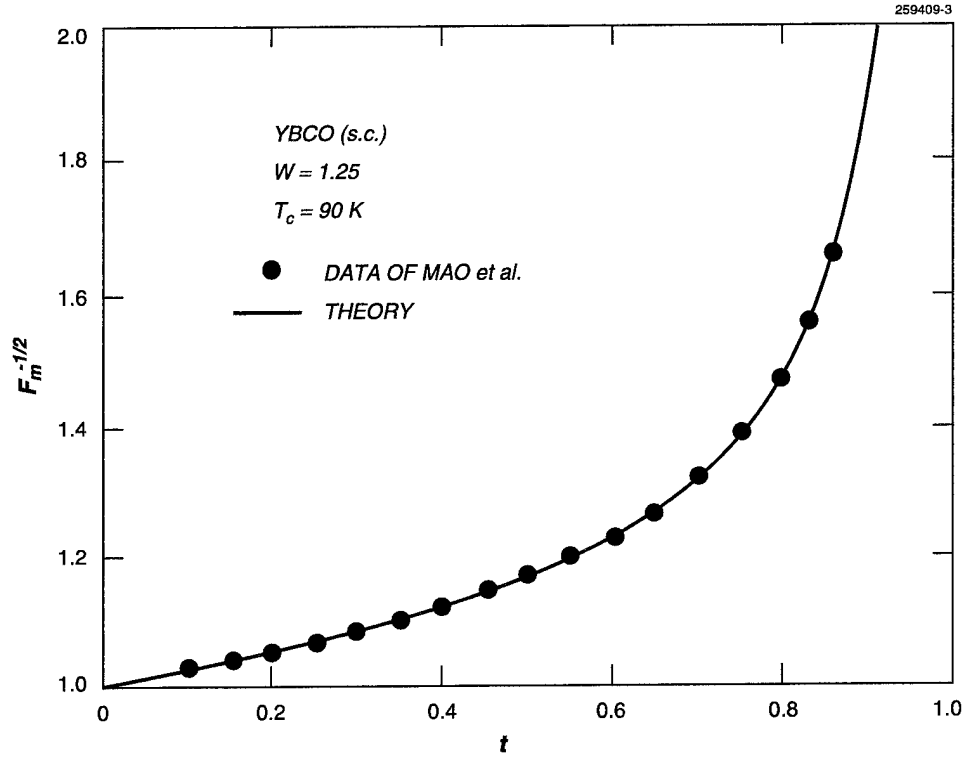


Figure 5. Penetration depth ratio $[n_{se}(0)/n_{se}(t)]^{1/2} (= F_m^{-1/2})$ as a function of t compared with s.c. data of Mao *et al.* [9] for YBCO with $W = 1.29$ and $T_c = 90 \text{ K}$. Other parameter values used are the same as those for Figure 4.

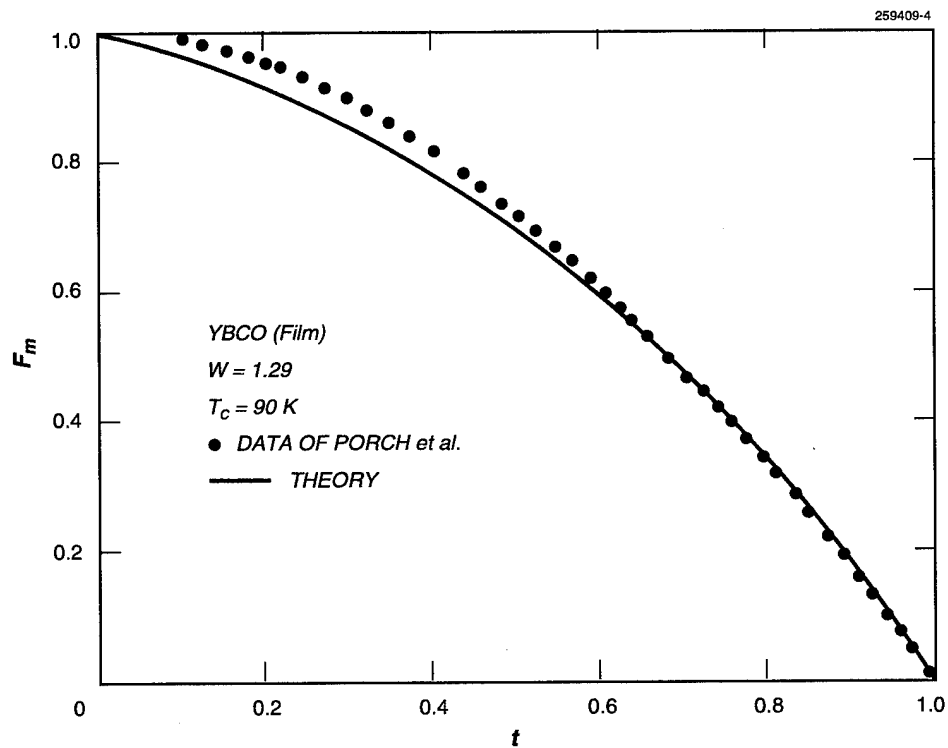


Figure 6. Two-fluid function F_m with phonon scattering included for $W = 1.29$, $T_c = 90 \text{ K}$, and $m = 4$. Data are from a highly textured YBCO film as reported by Porch *et al.* [10].

TABLE 2
Parameters for Calculations in Figures 2 through 8

Sample	Type	m —	ξ/x ($\times 10^{-3}$)	E_{hop} (meV)	T_c (K)	W	Ref
YBCO	crystal	8	5.2	10	93	1.25	8
YBCO	crystal	8	5.2	10	90	1.29	9
YBCO	text. film	4	5.2	10	90	1.29	10
YBCO	text. film	3	5.2	10	87	1.33	11,12
NbN	gran. film	2	5.2*	2.7 [†]	11.9	1.76 [‡]	13
TBCCO ($\text{Ti}_2\text{Ba}_2\text{CaCu}_2\text{O}_8$)	text. film	3	5.2	12	105	1.32	14
<p>*Undoubtedly, x is larger for this compound, but ξ is probably also larger because of a smaller phonon velocity.</p> <p>[†]Value consistent with $W = 1.76$ and $T_c = 11.9$ K.</p> <p>[‡]Value based on typical Bardeen-Cooper-Schrieffer (BCS) gap energies.</p>							

Another important property of superconductors that may be interpreted with this model is the critical current density i_c , usually measured as a transport current and divided by the cross-sectional area of the specimen or film. In the most recent study of CET [2], i_c was related to the effective supercarrier density of a thin film according to $n_{se}^{3/2}$. If this model is combined with the preceding results for $n_{se}(t)$, the following is obtained:

$$\frac{i_c(t)}{i_c(0)} = F_m^{3/2} \quad (18)$$

In Figure 7, Equation (18) is plotted for thin film $\text{YBa}_2\text{Cu}_3\text{O}_7$, and data used in earlier work [11,12] are replotted to show a substantially improved fit with theory, in this case with a lower value of $m = 3$ that appears to produce a better fit to textured film specimen data. For an additional test of the theory, the case of the BCS superconductor NbN ($T_c = 11.9$ K) is plotted for $W = 1.76$, and $m = 2$ (granular film) together with experimental points of Clem et al. [13]. Another set of data [14] from commercial TBCCO with $T_c = 105$ K plotted in logarithmic form in Figure 8 compares excellently with theory.

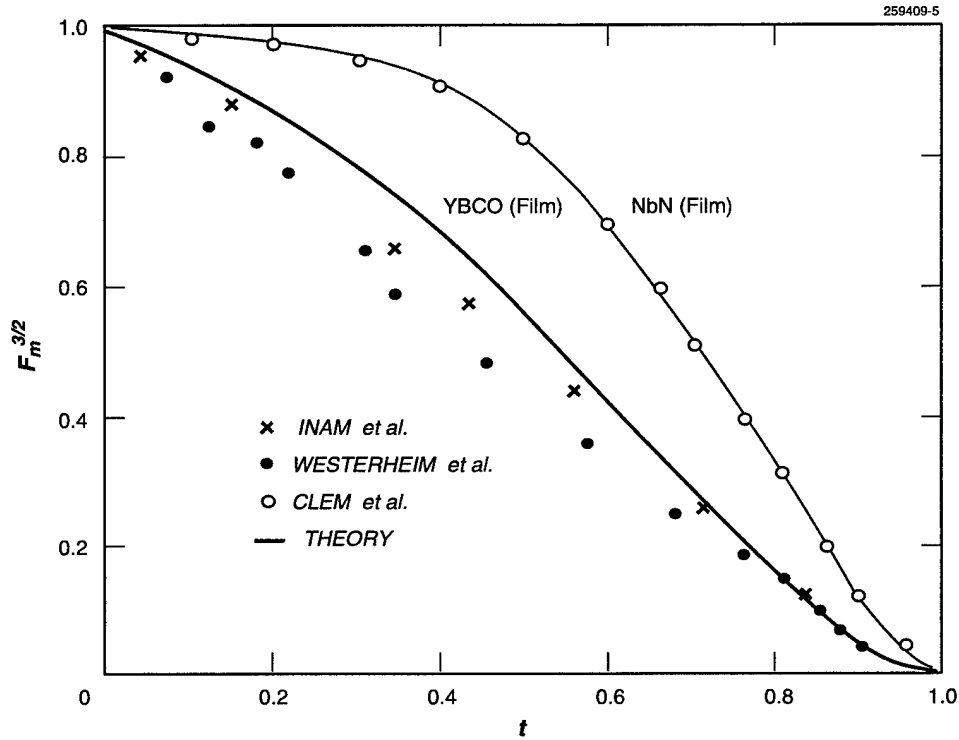


Figure 7. Reduced critical current density $i_c(t)/i_c(0)$ as a function of t for YBCO thin films, with $W = 1.33$ and $T_c = 87$ K. Data are from Westerheim et al. [11] and Inam et al. [12]. The second calculated curve is for NbN with $W = 1.76$, the BCS value, compared with data of Clem et al. [13]. For the oriented films of YBCO, $m = 3$; for the granular film of NbN, m is reduced to 2.

Another exercise of interest is to apply this new model to a point on the (proposed) optimum case curve E of Figure 1 to estimate the effects of the likely trade-offs between T_c and i_c as the critical temperature increases. To this end Equation (18) is plotted in Figure 9 for parameter values of $\beta = 0$, $x = 0.25$, and $m = 8$. Here W is reduced to 0.46 because T_c is raised to 300 K, and E_{hop} remains at 12 meV. The reduced i_c curve for s.c. YBCO with $T_c = 93$ K and $W = 1.25$ is plotted to illustrate the advantage in current capability at $T = 77$ K, where i_c is more than three times greater for the 300-K superconductor.

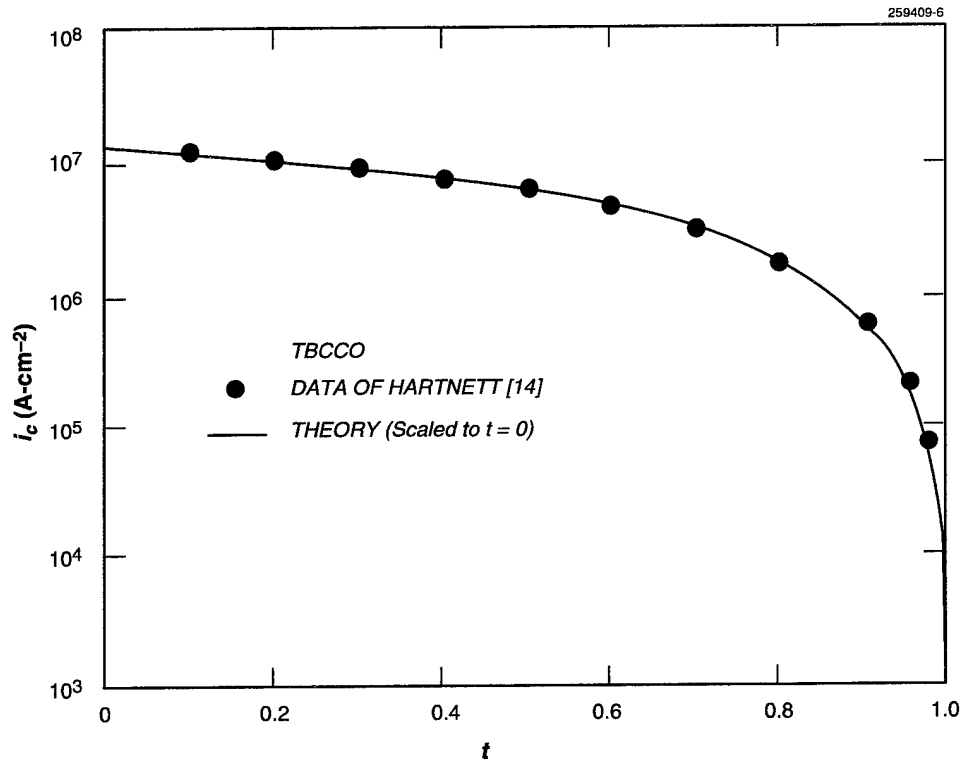


Figure 8. Logarithmic plot of $i_c(t)$ versus t for parameters of Figure 5 but with $W = 1.32$ and $T_c = 105$ K. Data are for TBCCO [14].

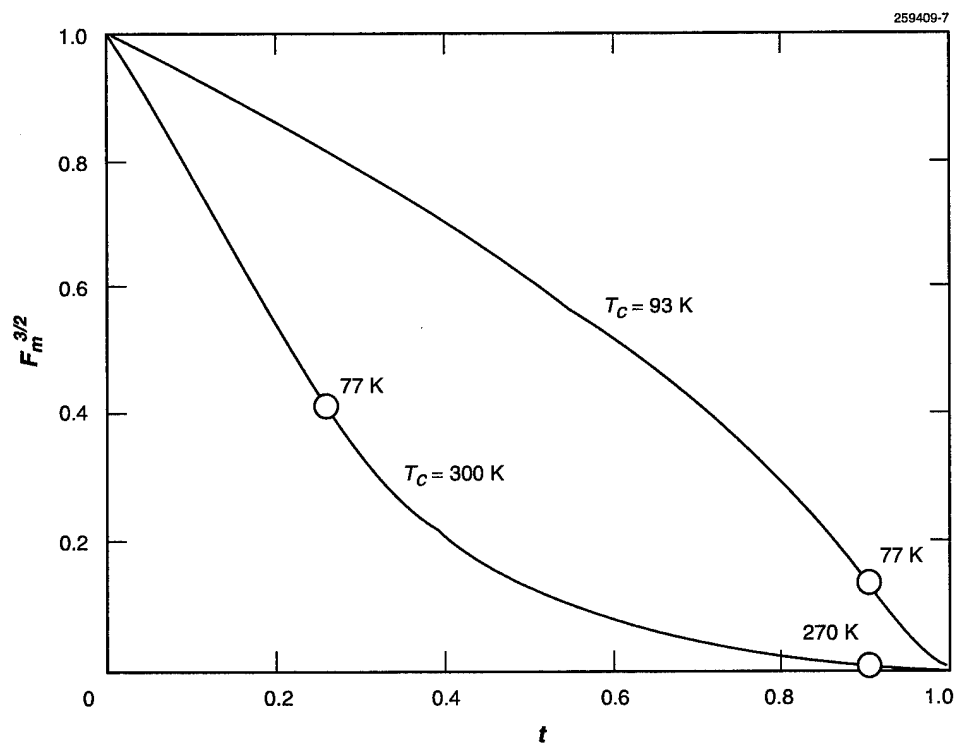


Figure 9. Comparison of $i_c(t)/i_c(0)$ versus t for standard YBCO with a postulated 300-K cuprate superconductor. In both cases, $m = 8$, the value for high quality single crystals.

5. DISCUSSION

Refinements to the CET model for determining T_c indicate that hopping electron activation energies should be more than double (>10 meV) those reported in the original work [1,2] and are directly dependent on the strength of the axial crystal-field component around the Cu ions. As concluded in the initial work on this theoretical approach [1], critical temperatures could exceed 300 K through the attainment of ideal dispersal ($\beta \rightarrow 0$) and larger activation energies. Reports of superconductivity behavior at temperatures near 250 K [15] in cuprates prepared by a sequential epitaxial layer growth technique support the earlier suggestion that large E_{hop} values obtained from planar oxygen coordinations and nearly perfect cation or vacancy dispersals by some type of individual layer deposition method could lead to optimized cuprate superconductor structures.

The influence of phonon interactions on polaron charge transfer is characterized as an exponential factor that causes an additional decrease in the effective supercarrier density with increasing temperature. The simple two-fluid model derived from this theory has also been generalized to describe variations in the growth of supercurrent near T_c . One notable result of this analysis is that the variation of supercarrier density with temperature becomes linear at temperatures near zero if T_c is large and the material is in the form of a high quality single crystal. For textured films there is evidence that the linear relation does not hold at low temperatures, possibly because of a nonlinear relation between the mean phonon wavelength and temperature due to the presence of grain boundaries and submicrometer film thicknesses. For lower- T_c materials, metals for example, the temperature dependence returns to the exponential behavior predicted by the earlier model without lattice scattering effects or that typical of the BCS theory. In these cases, the two-fluid universal curves would resemble those of Figure 3 rather than Figure 4 at lower values of t .

As a consequence, higher- T_c materials would have supercurrent capacities that are more vulnerable to lattice vibrations near their highest operating temperatures. From the calculated curves plotted in Figure 9, the relative supercarrier density at 90% of T_c for a material with $T_c = 300$ K is only a small fraction of that for YBCO with $T_c = 93$ K. Nonetheless, there is a substantial advantage to higher critical temperatures for operation in the lower temperature regimes. A 300-K superconductor engineered from these systems, for example, theoretically would have almost a fourfold advantage in i_c over YBCO if operated at 77 K. If a system could be found with a greater E_{hop} , the W parameter, hence the $i_c(t)$ curve, would be correspondingly higher.

With these revisions to the CET theory, the parameter trends for the design of a hypothetical superconductor with optimum properties are reexamined. To achieve the highest T_c , b should be as large as possible and E_{hop} as large as tolerable (bearing in mind the implications of magnetic exchange trap contributions to E_{hop} and the spin-alignment frustration requirement discussed in Dionne [2]). These conditions will permit a corresponding increase in ΔE to preserve a reasonably small Ω ($= \Delta E/b$) and maintain a low threshold polaron density x_t . (In low- T_c metals, for which b is small because of the lower ionization potentials of the outer electrons, x_t can be large [2]). If ΔE is raised through a decrease in temperature, there is an additional benefit of an increase in the condensation energy ΔG as determined

by the ferroelectric alignment of polarons [2]. With a larger ΔG , higher critical magnetic field and critical current densities would result. Finally, to reduce the effect of lattice vibration scattering of coherent polarons, an increased acoustic phonon velocity is desired, requiring high stiffness and low mass density.

The layered cuprates are only partially covalent, and their dielectric constants, although lower than those of metals and intermetallics, are still relatively high, particularly in the larger cation compounds in which superconductivity has been found. There are, however, other possible vehicles for large polaron superconductivity. Recent work in polymers [16] may provide advances in this field, particularly in view of their high covalency, low dielectric constants, and lower mass densities.

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